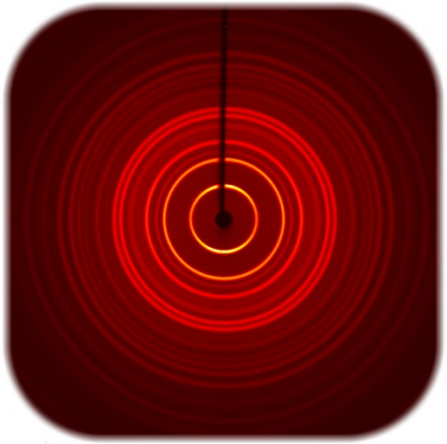


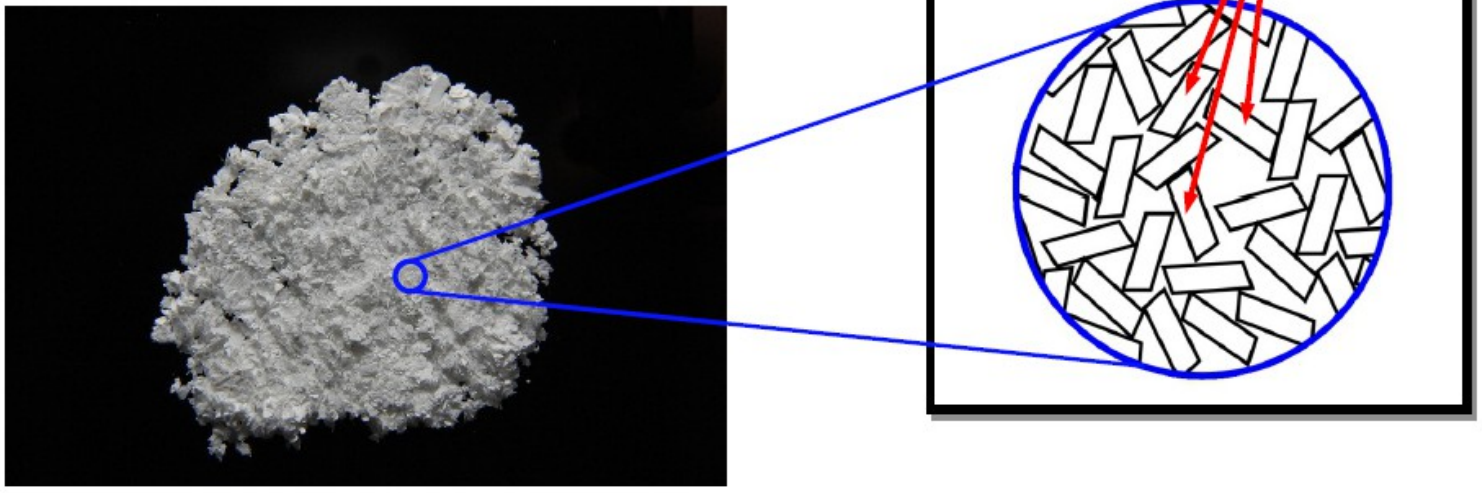
Extraction of intensities from powder diffraction pattern

Important step before solving the crystal structure

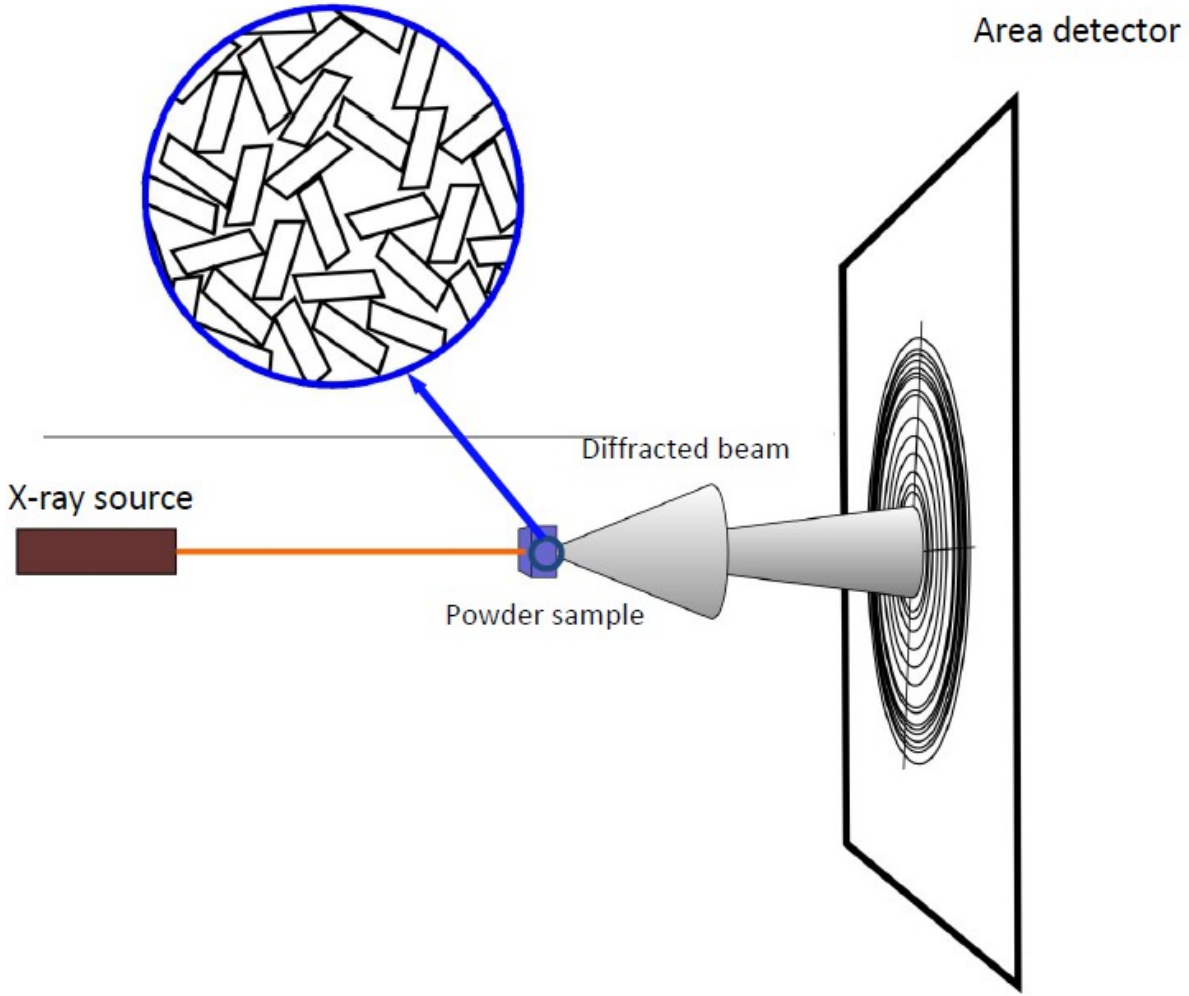
Sample

Powder sample = polycrystalline material

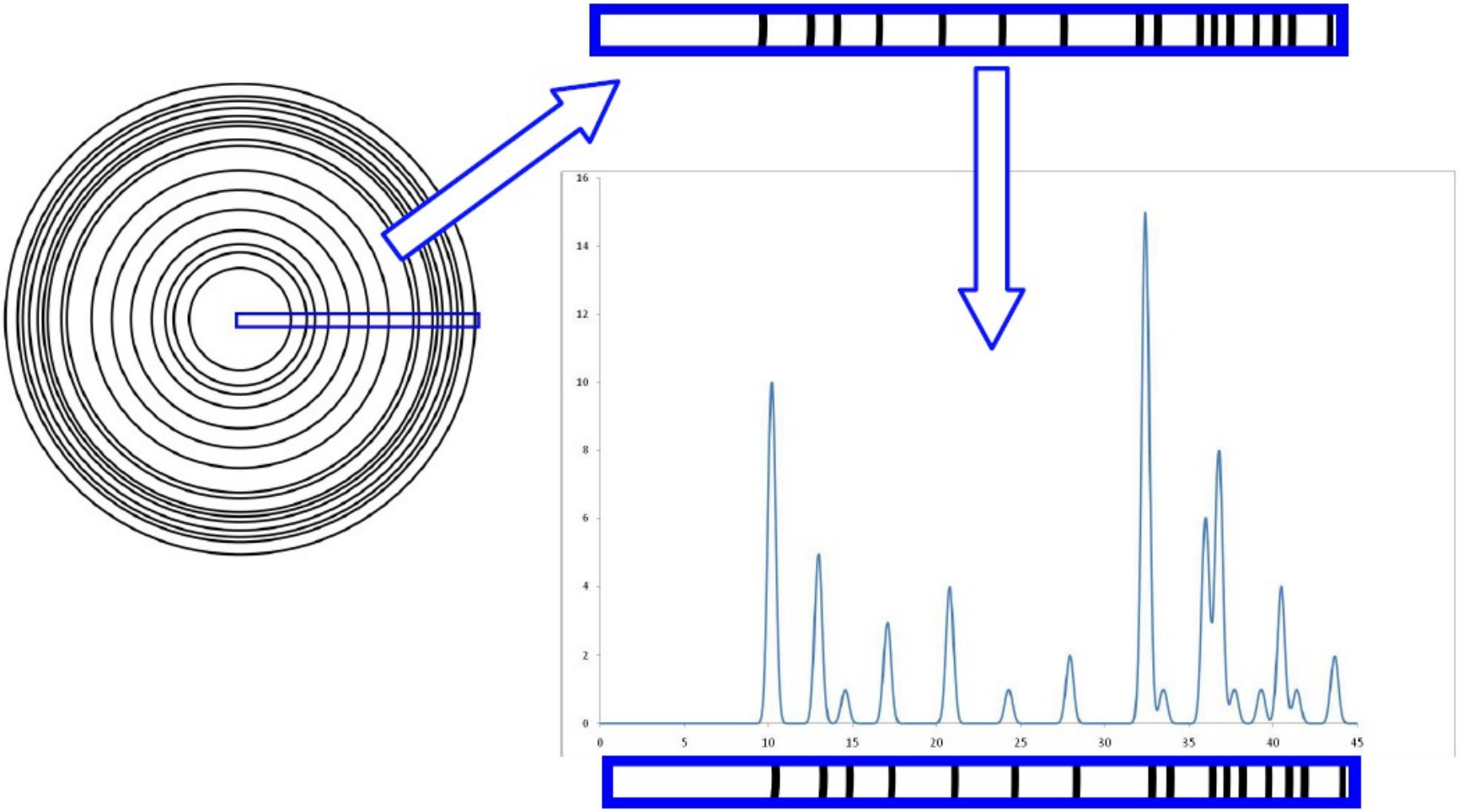
Size of crystals is around 10^{-6}m



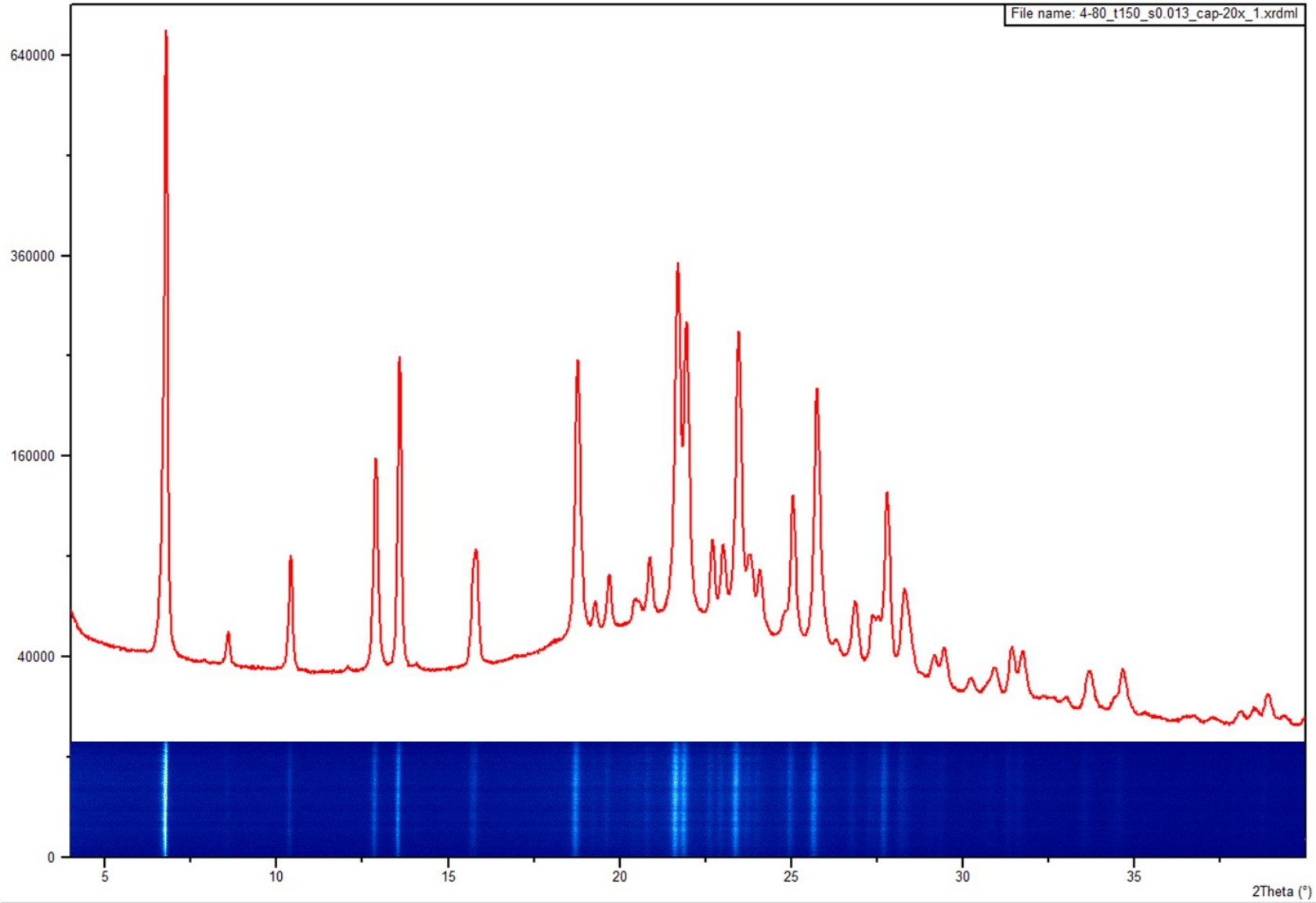
Diffraction of the powder sample



Diffraction of the powder sample



Diffraction of the powder sample

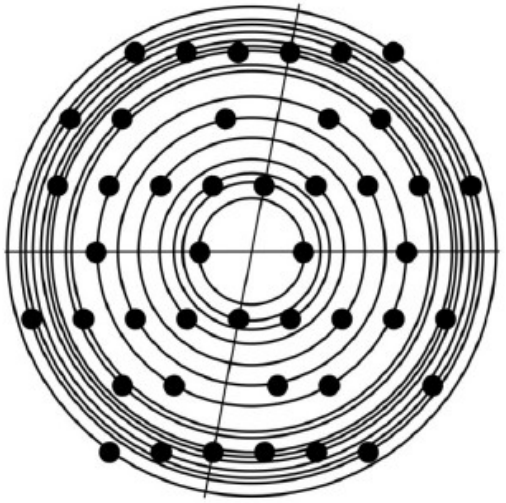


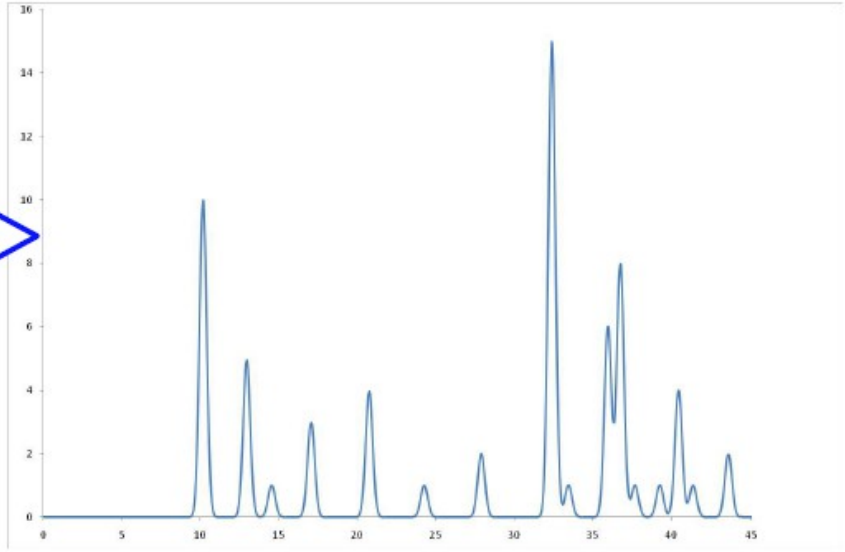
Diffraction of the powder sample

- Information loss – powder pattern is a 1D projection of 3D reciprocal space

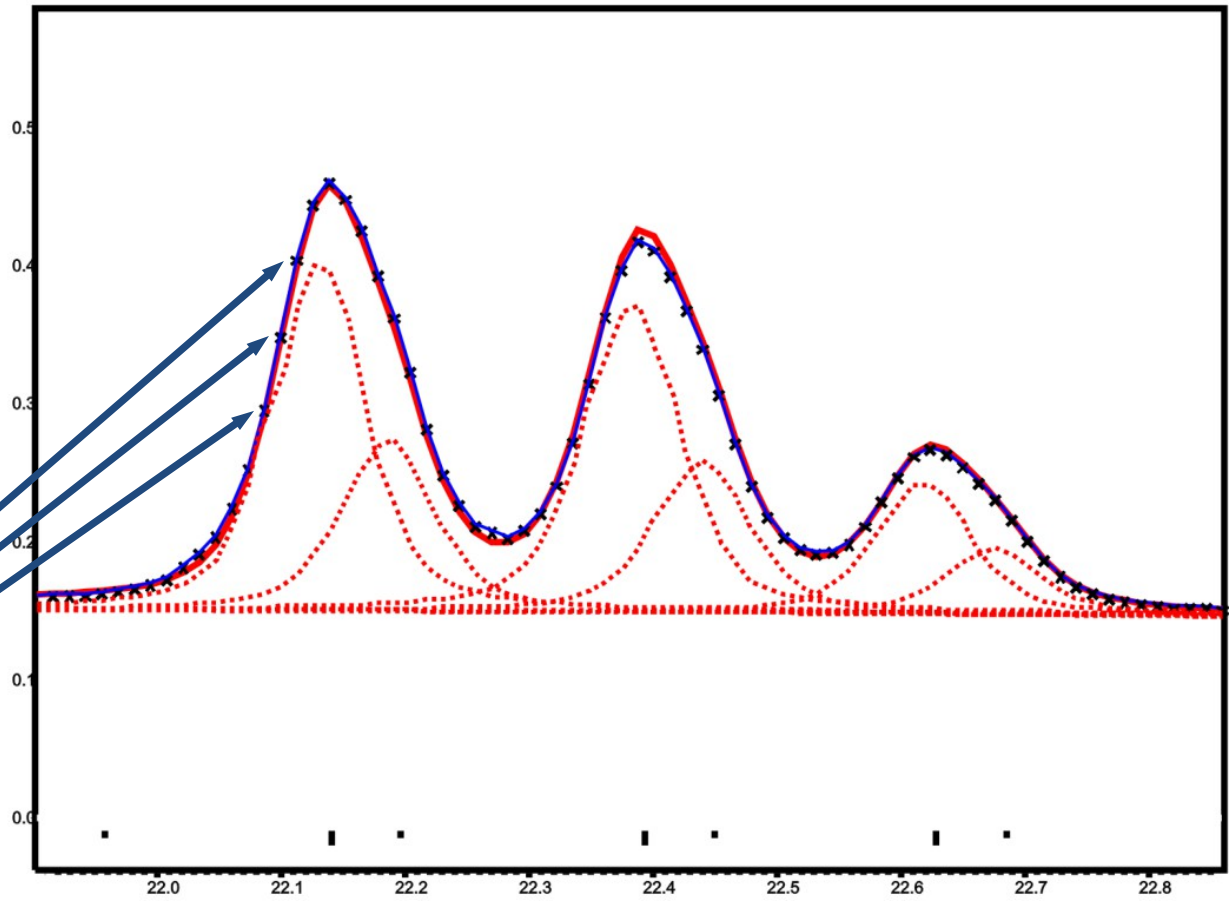
How to describe peak shapes?

How to get intensities?





Powder pattern



Intenzita v každém bodě záznamu

$$y_{ci} = s \sum_h L_h |F_h|^2 \delta(2\theta_i - 2\theta_h) P_h A + y_{bi}$$

s – scale factor, $\mathbf{L_h}$ – Lorentz, polarization and multiplicity factor,

$\mathbf{F_h}$ – structure factor, **δ** – reflection profile, $\mathbf{P_h}$ – preferred orientation function, **A** – absorption factor, $\mathbf{y_{bi}}$ - background

Powder pattern

$$y_{ci} = s \sum_h L_h |F_h|^2 \delta(2\theta_i - 2\theta_h) P_h A + y_{bi}$$

$$|F_h|^2 \approx I$$

$$G(b_G, x) = \frac{1}{\sqrt{2\pi} b_G} \exp\left(-x^2 / 2b_G^2\right)$$

$$L(b_L, x) = \frac{2}{\pi b_L} \frac{1}{1 + (2x/b_L)^2}$$

Unknown model – what is the intensity?

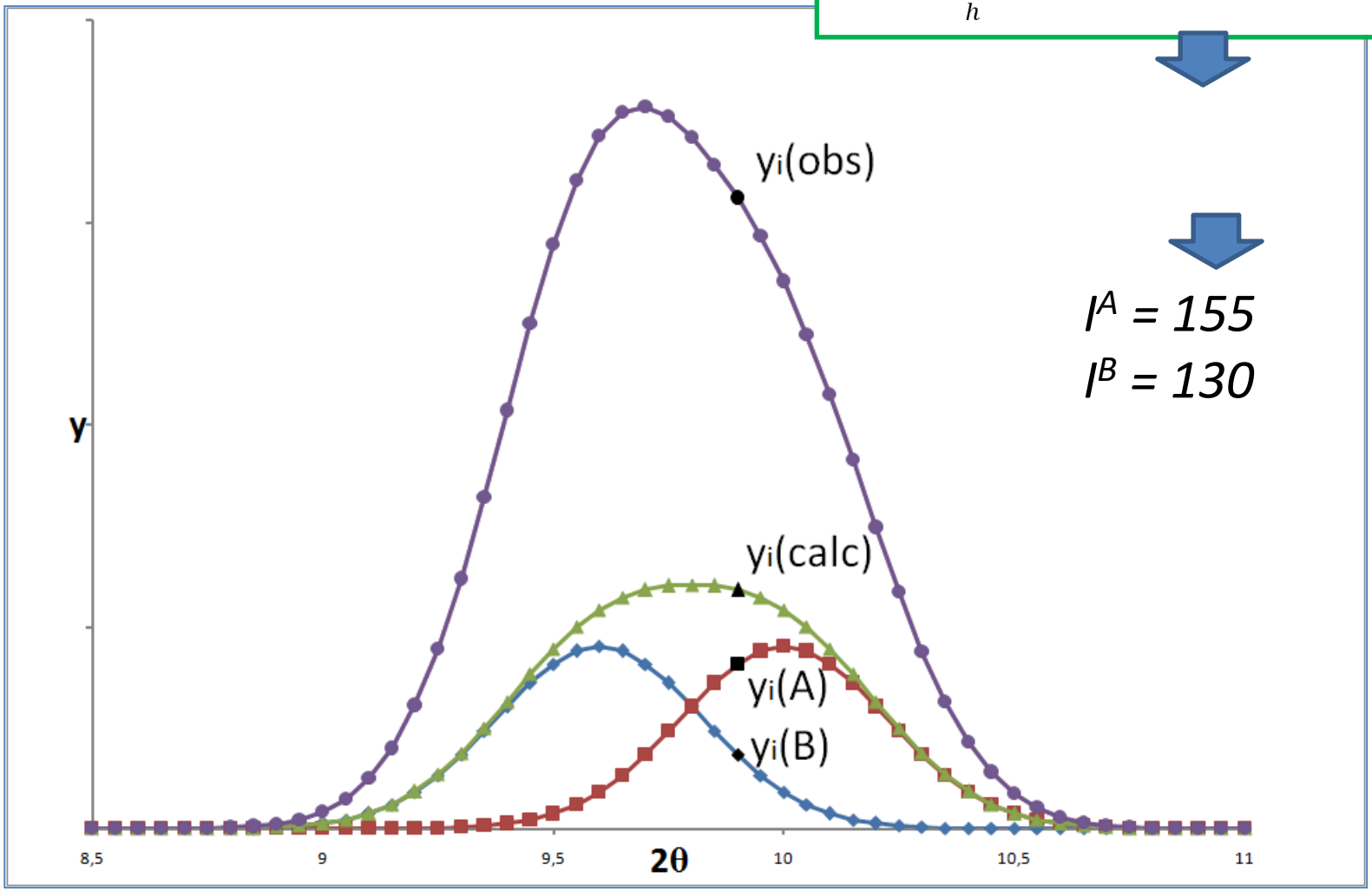
s – scale factor, $\mathbf{L_h}$ – Lorentz, polarization and multiplicity factor, $\mathbf{F_h}$ – structure factor, **δ** – reflection profile, $\mathbf{P_h}$ – preferred orientation function, **A** – absorption factor, $\mathbf{y_{bi}}$ - background

Le Bail method

$I^A = 50$

$I^B = 50$

$$y_{ci} = s \sum_h L_h |F_h|^2 \delta(2\theta_i - 2\theta_h) P_h A + y_{bi}$$

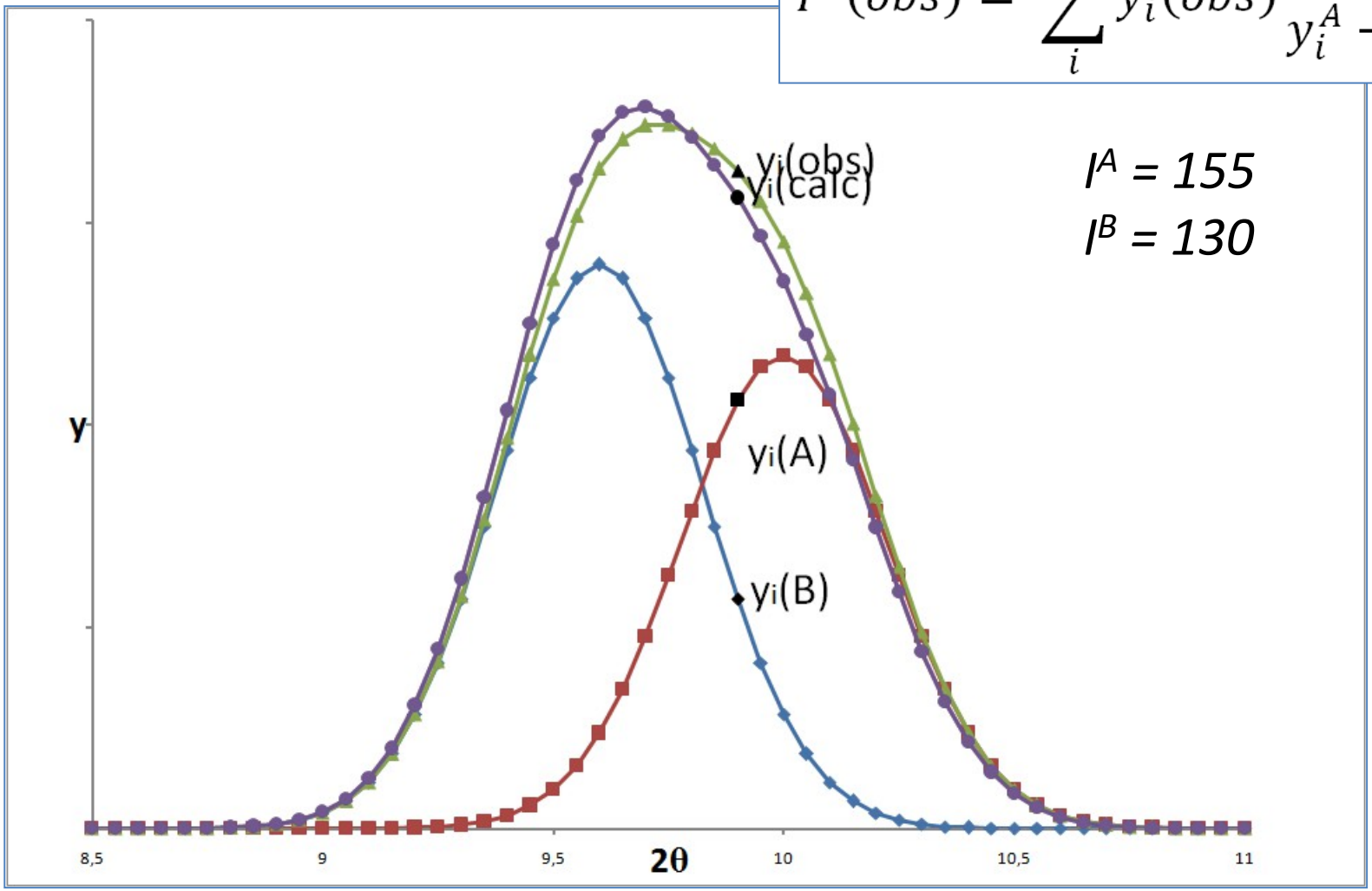


$I^A = 155$

$I^B = 130$

Le Bail method

$$I^A(obs) = \sum_i y_i(obs) \frac{y_i^A}{y_i^A + y_i^B}$$

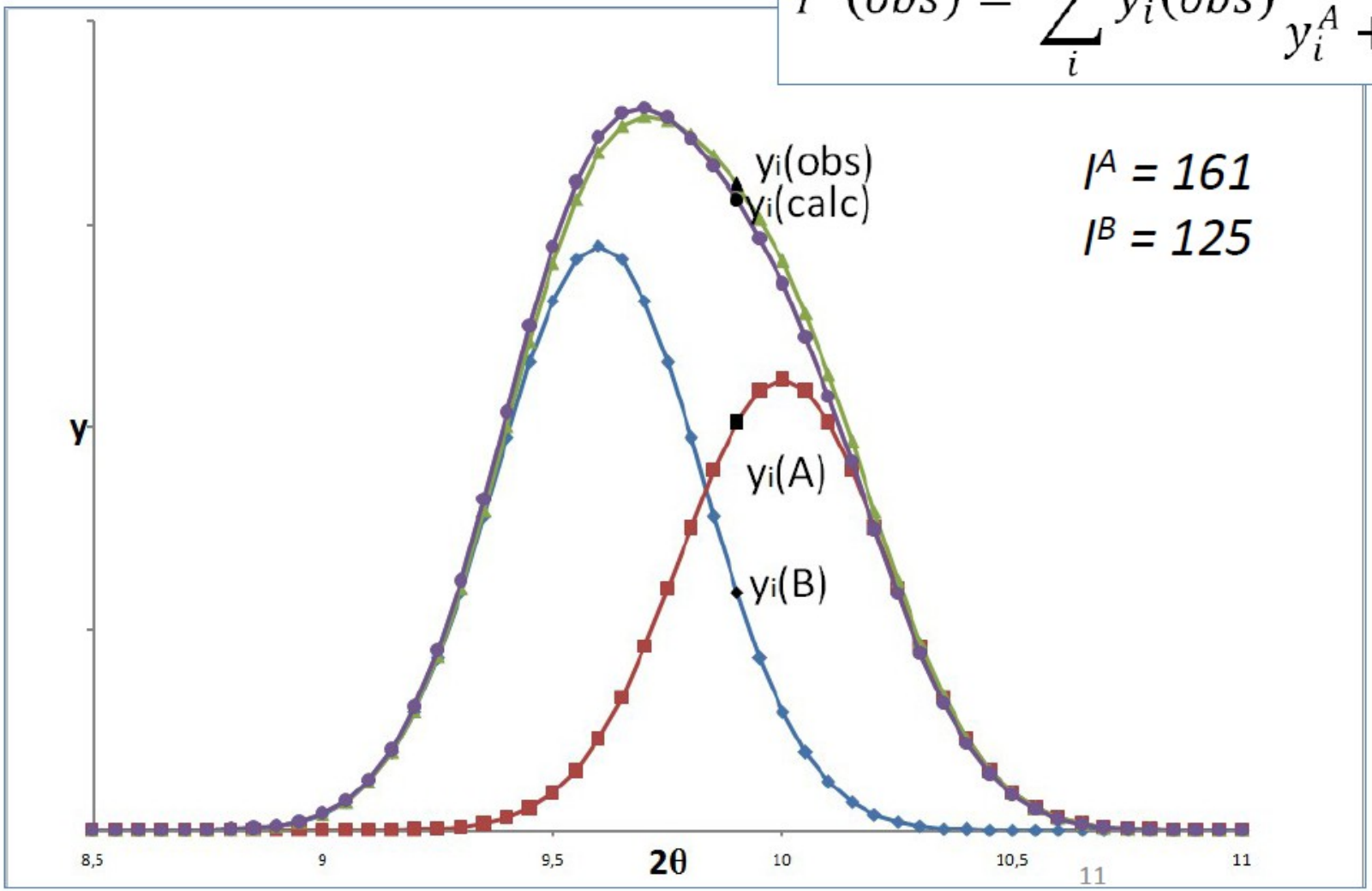


$I^A = 155$

$I^B = 130$

Le Bail method

$$I^A(obs) = \sum_i y_i(obs) \frac{y_i^A}{y_i^A + y_i^B}$$

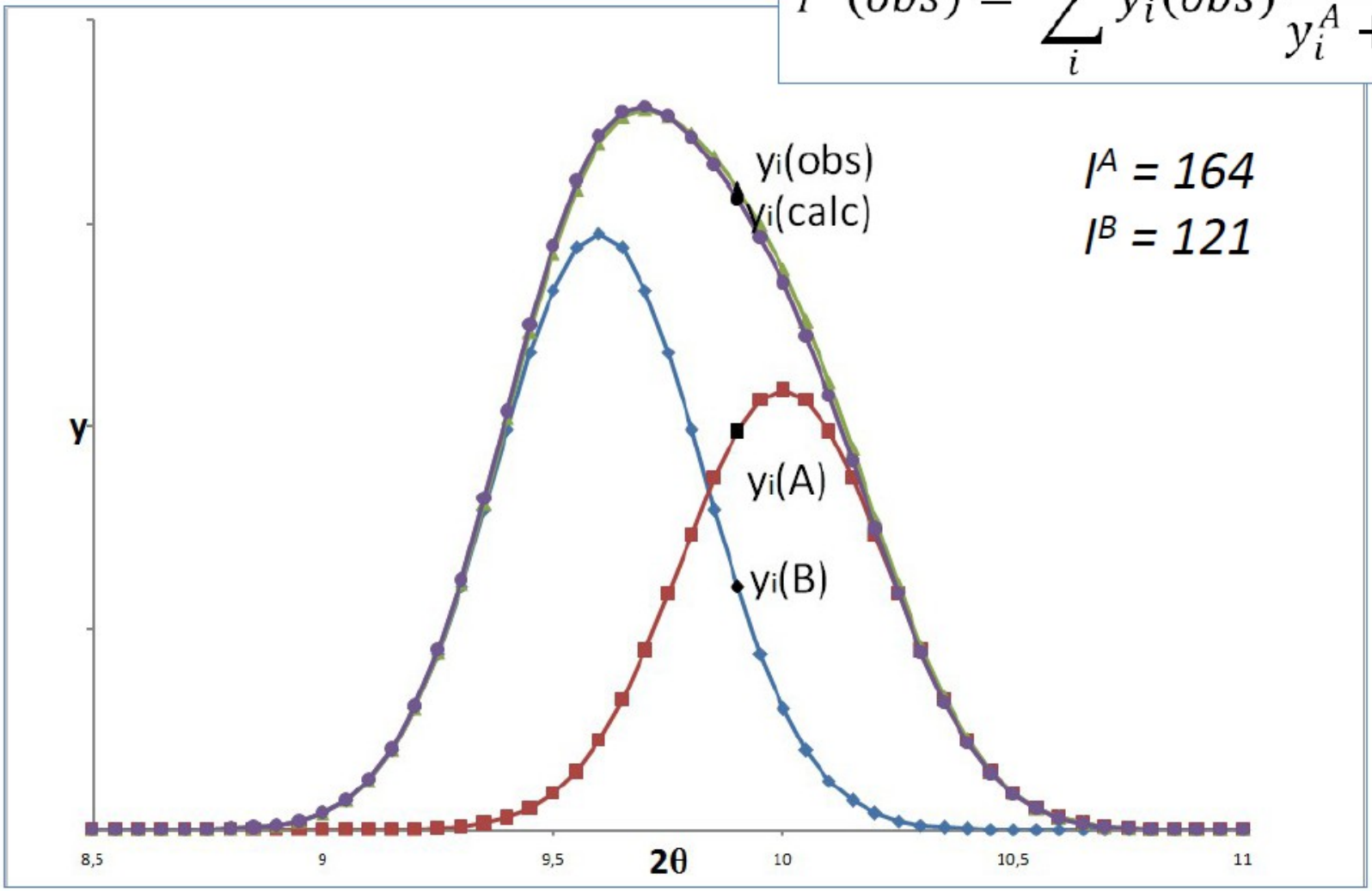


$I^A = 161$

$I^B = 125$

Le Bail method

$$I^A(obs) = \sum_i y_i(obs) \frac{y_i^A}{y_i^A + y_i^B}$$

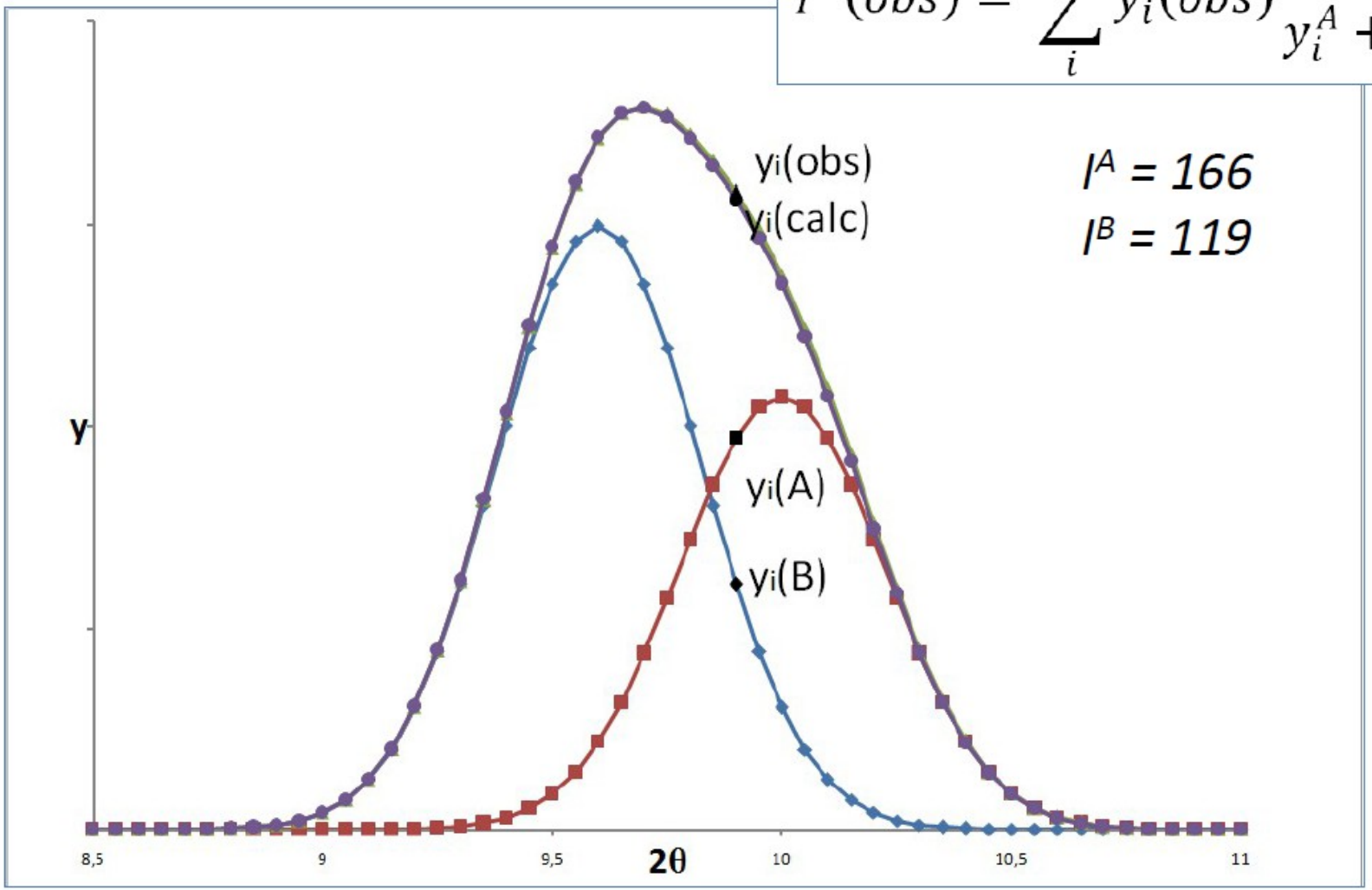


$I^A = 164$

$I^B = 121$

Le Bail method

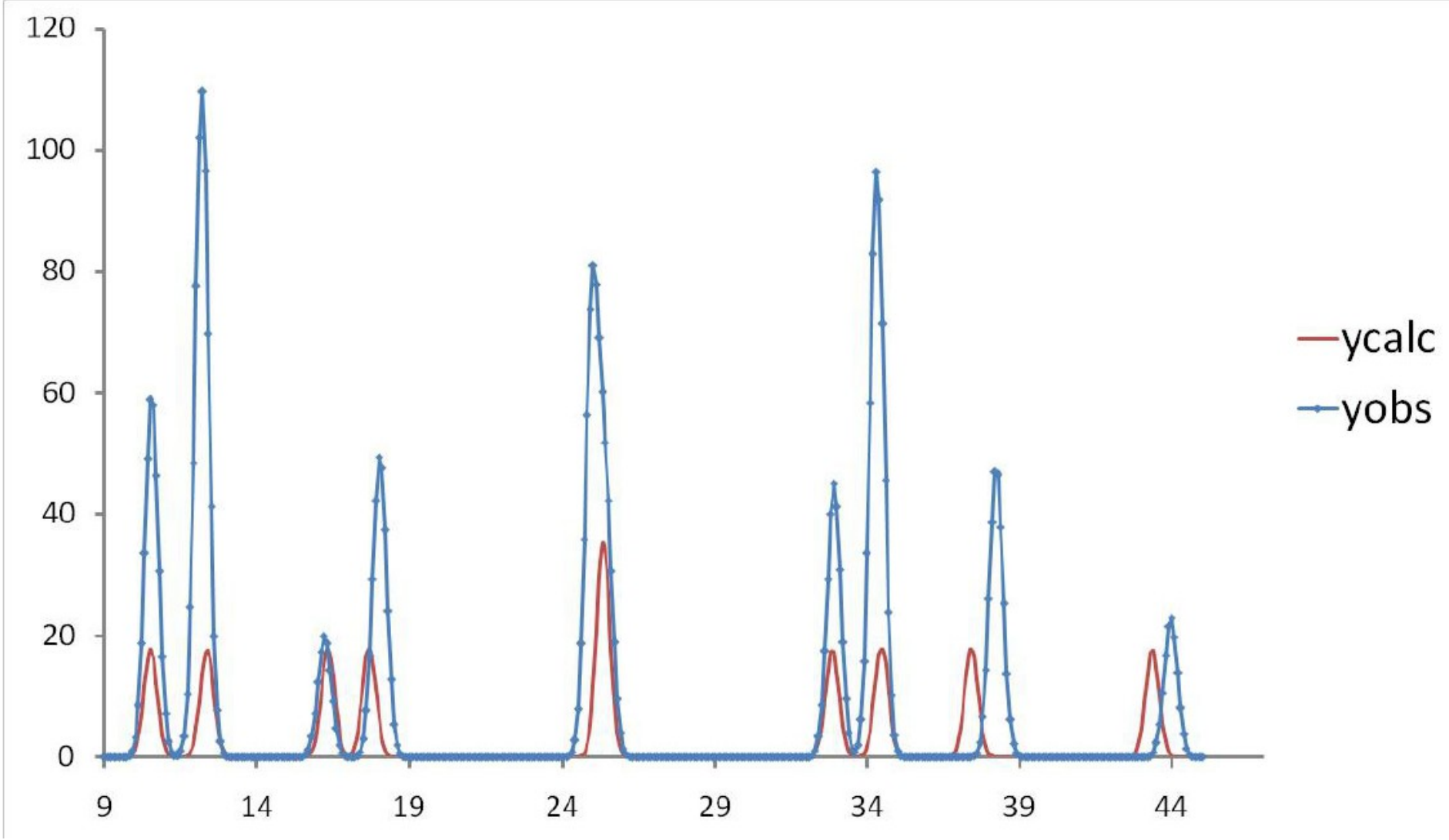
$$I^A(obs) = \sum_i y_i(obs) \frac{y_i^A}{y_i^A + y_i^B}$$



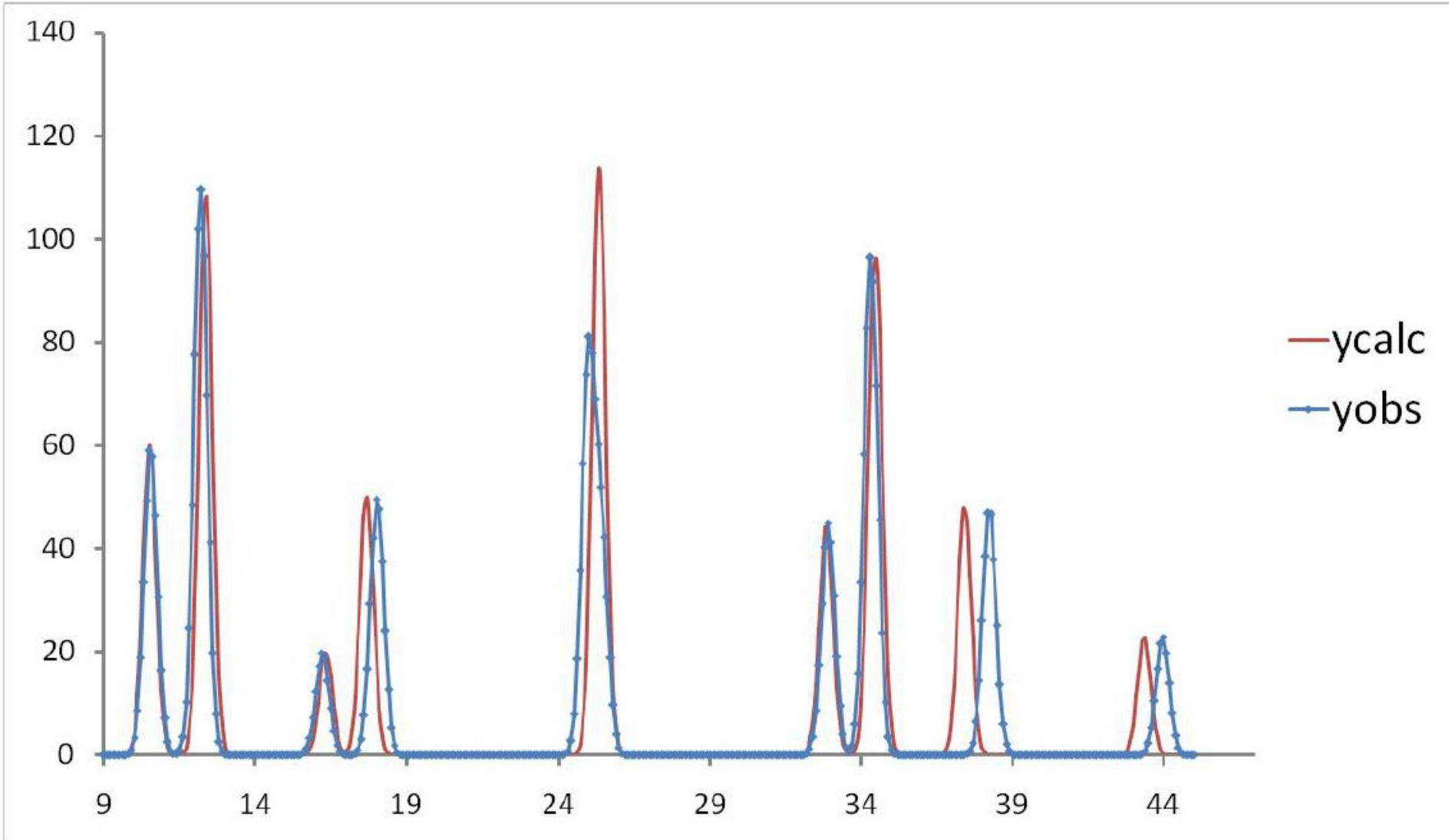
$I^A = 166$

$I^B = 119$

Le Bail method

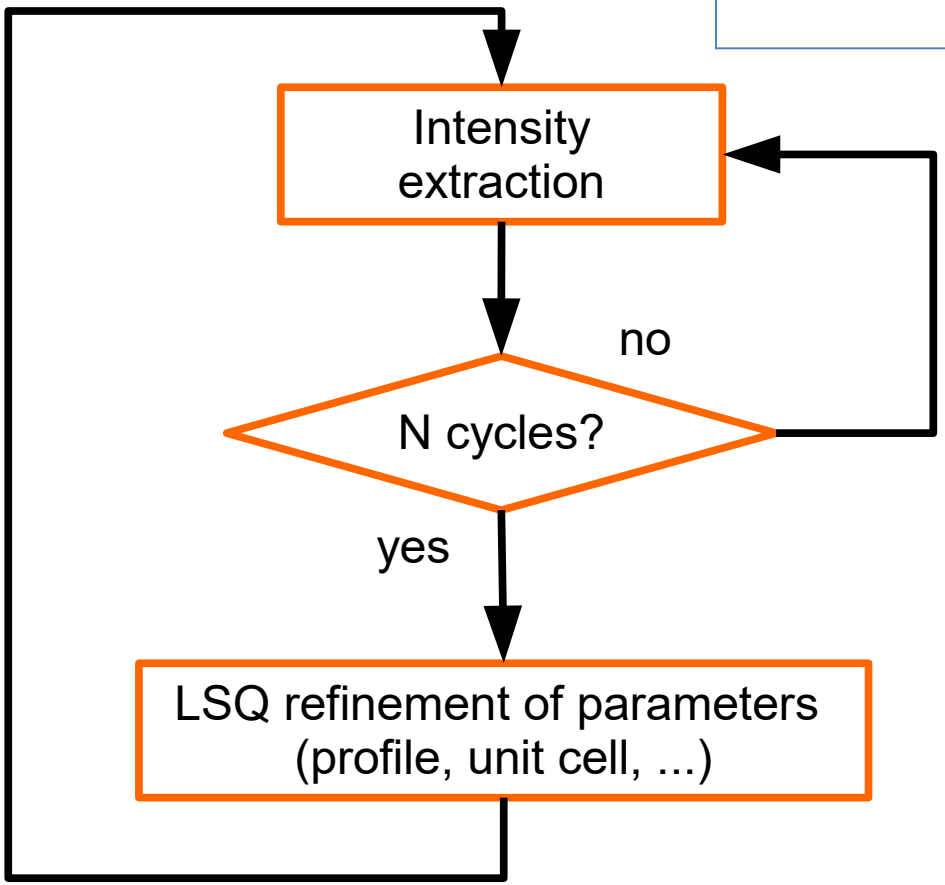


Le Bail method



Le Bail method

$$I^A(obs) = \sum_i y_i(obs) \frac{y_i^A}{y_i^A + y_i^B}$$



Refinement of profile and unit cell parameters by least squares methods combined with the calculation of peak's intensities

Profile parameters

Gaussian:

$$G(b_G, x) = \frac{1}{b_G\sqrt{2\pi}} \exp\left(-x^2 / 2b_G^2\right)$$

$$b_G^2 = \frac{H_G^2}{8\ln 2}$$

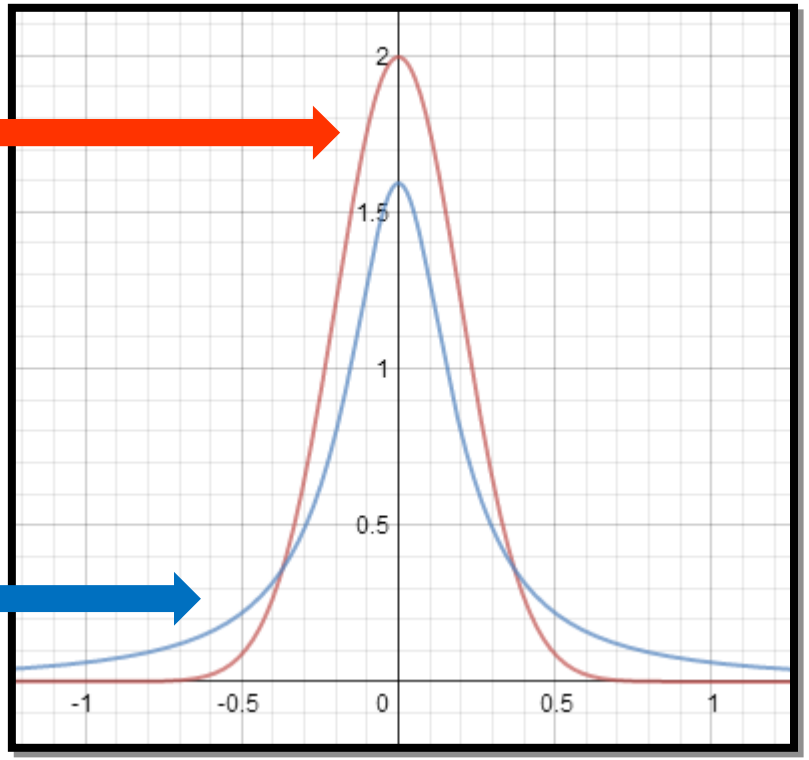
where H_G is „width“ of the peak

Lorentzian:

$$L(b_L, x) = \frac{2}{\pi b_L} \frac{1}{1 + (2x/b_L)^2}$$

$$b_L = H_L$$

where H_L is „width“ of the peak



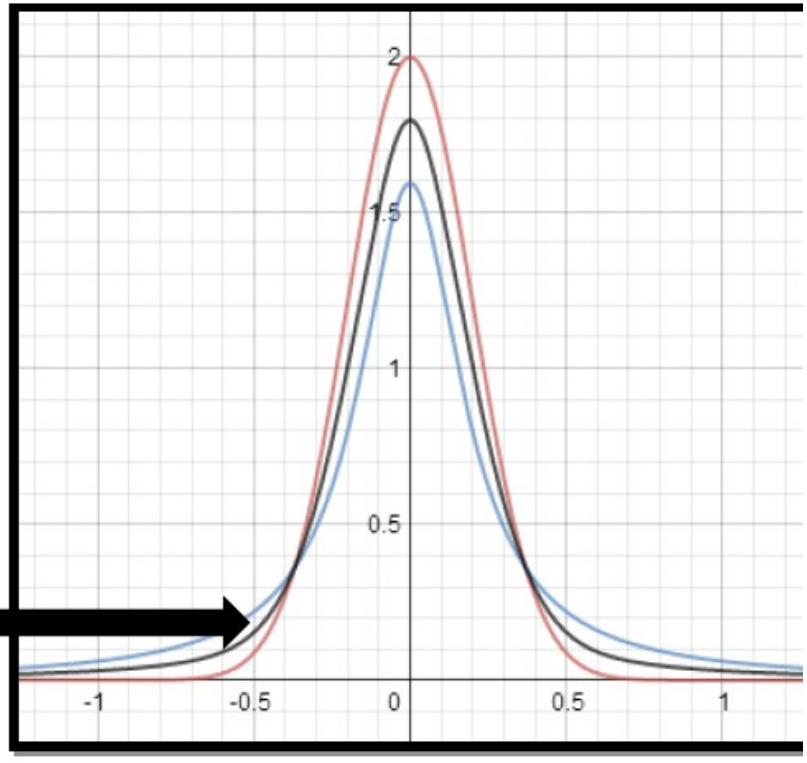
Profile parameters

Voigt function:

$$V(b_G, b_L, x) = \int_{-\infty}^{+\infty} G(b_G, x') L(b_L, x - x') dx'$$

It is a combination of **Gaussian** and **Lorentzian**. For the description of powder profiles, we are using pseudo-voigt function:

$$pV(H, x) = \eta L(H, x) + (1 - \eta) G(H, x)$$



Profile parameters

For gaussian, we are usually using parameters according to Cagliotti, Pauletti & Ricci, 1958 (Nucl.Instrum., **3**, 223):

$$b_G^2 = U\tan^2\theta + V\tan\theta + W + \frac{P}{\cos^2\theta}$$

Because there is an equation:

$$\tan^2\theta + 1 = \frac{1}{\cos^2\theta}$$

It means, that these parameters U, W, P are strongly correlating

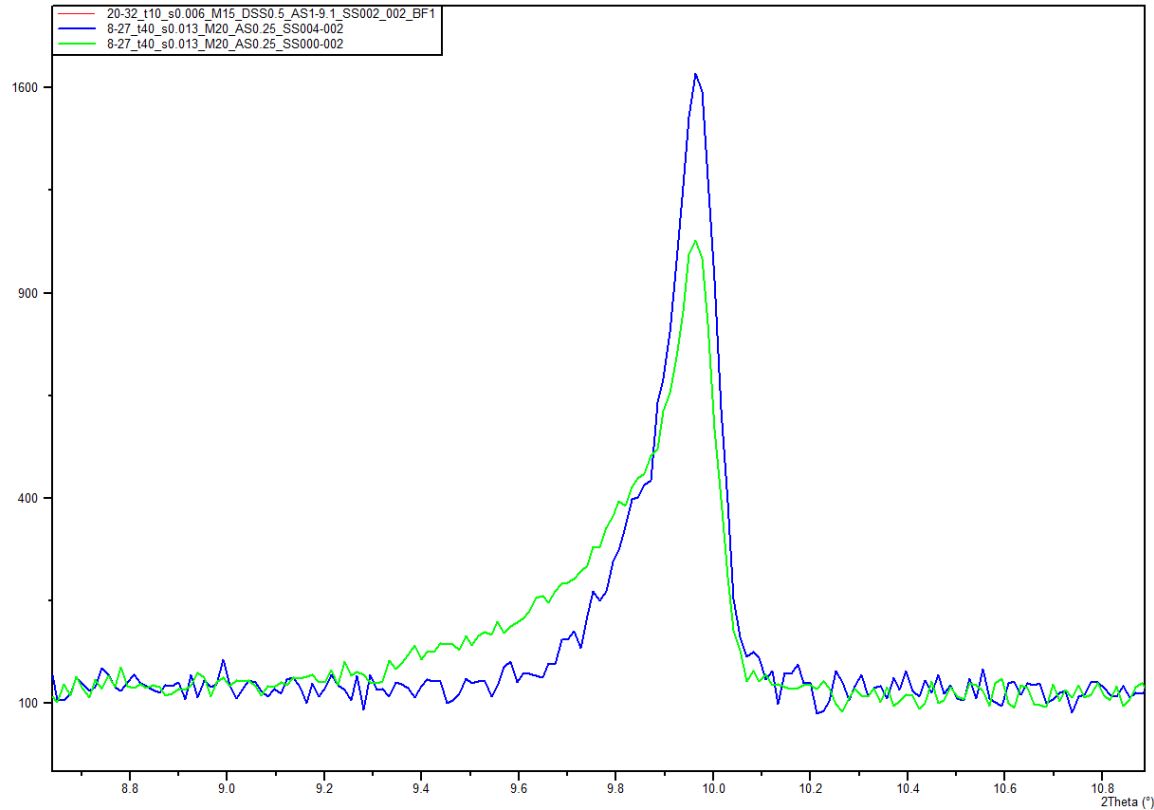
For Lorentzian, we are using:

$$b_L = X_L/\cos\theta + Y_L\tan\theta$$

Asymmetry

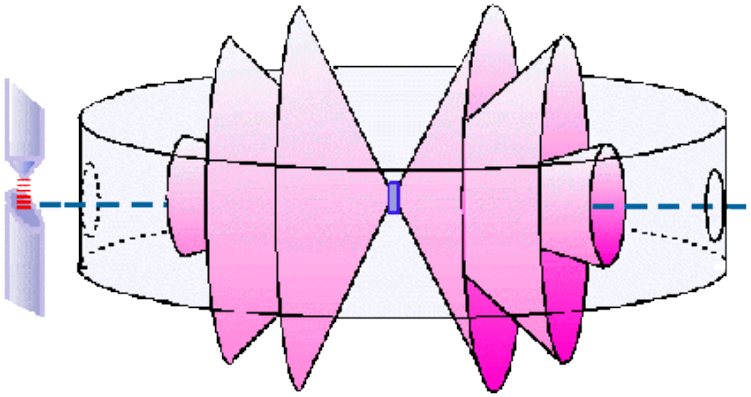
- Asymmetry is caused by the fact, that beam source, sample and detector have non-zero dimensions.

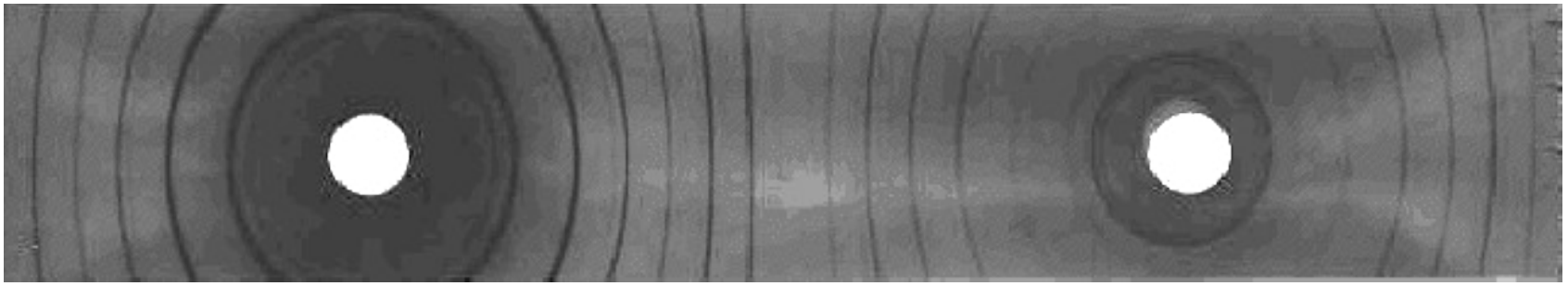
It is possible to correct it by:
- smaller slits
- soller's slits



Asymmetry

- Influence of the detector's size



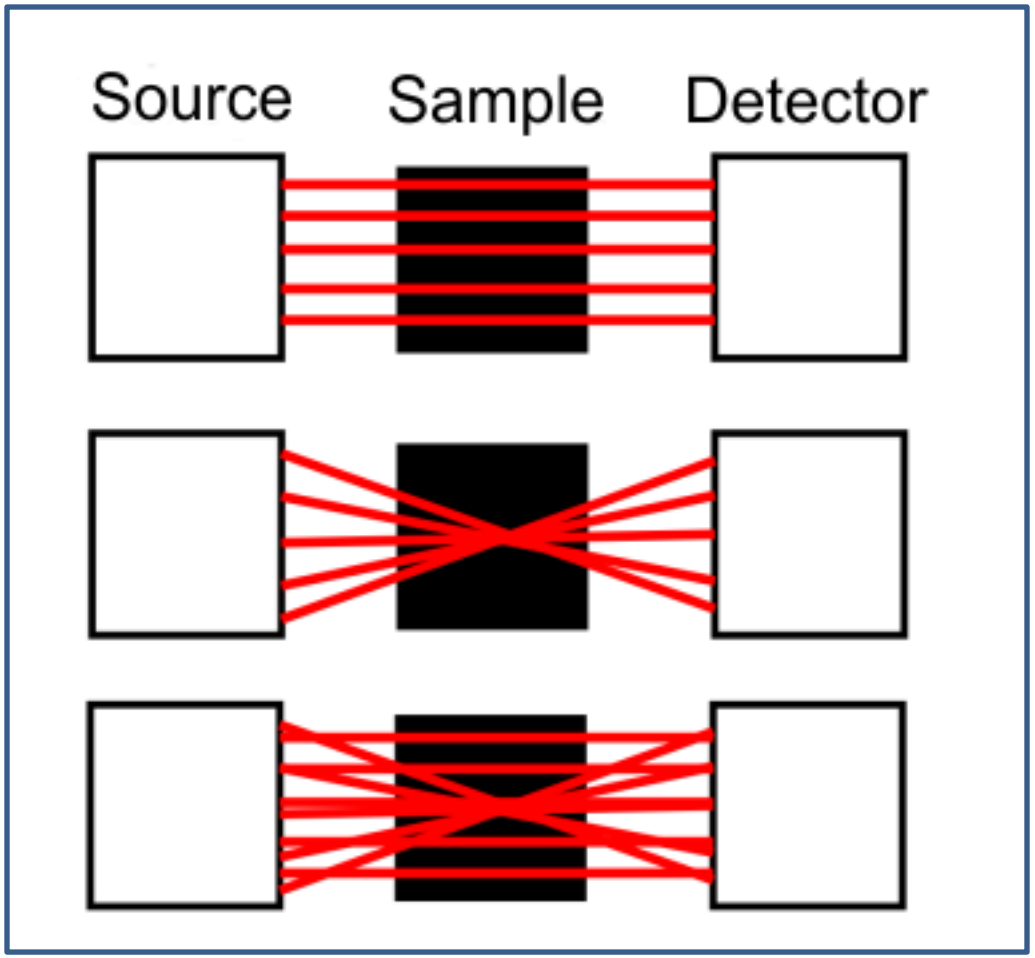


http://www.chemgapedia.de/vsengine/vlu/vsc/de/ch/11/aac/vorlesung/kap_5/vlu/kristallstrukturanalyse.vlu/Page/vsc/de/ch/11/aac/vorlesung/kap_5/kap5_7/kap57_2.vscml.html

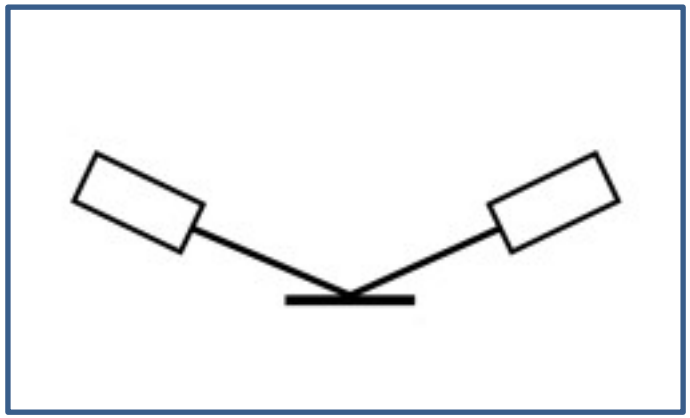
Asymmetry

- Influence of the source and sample size

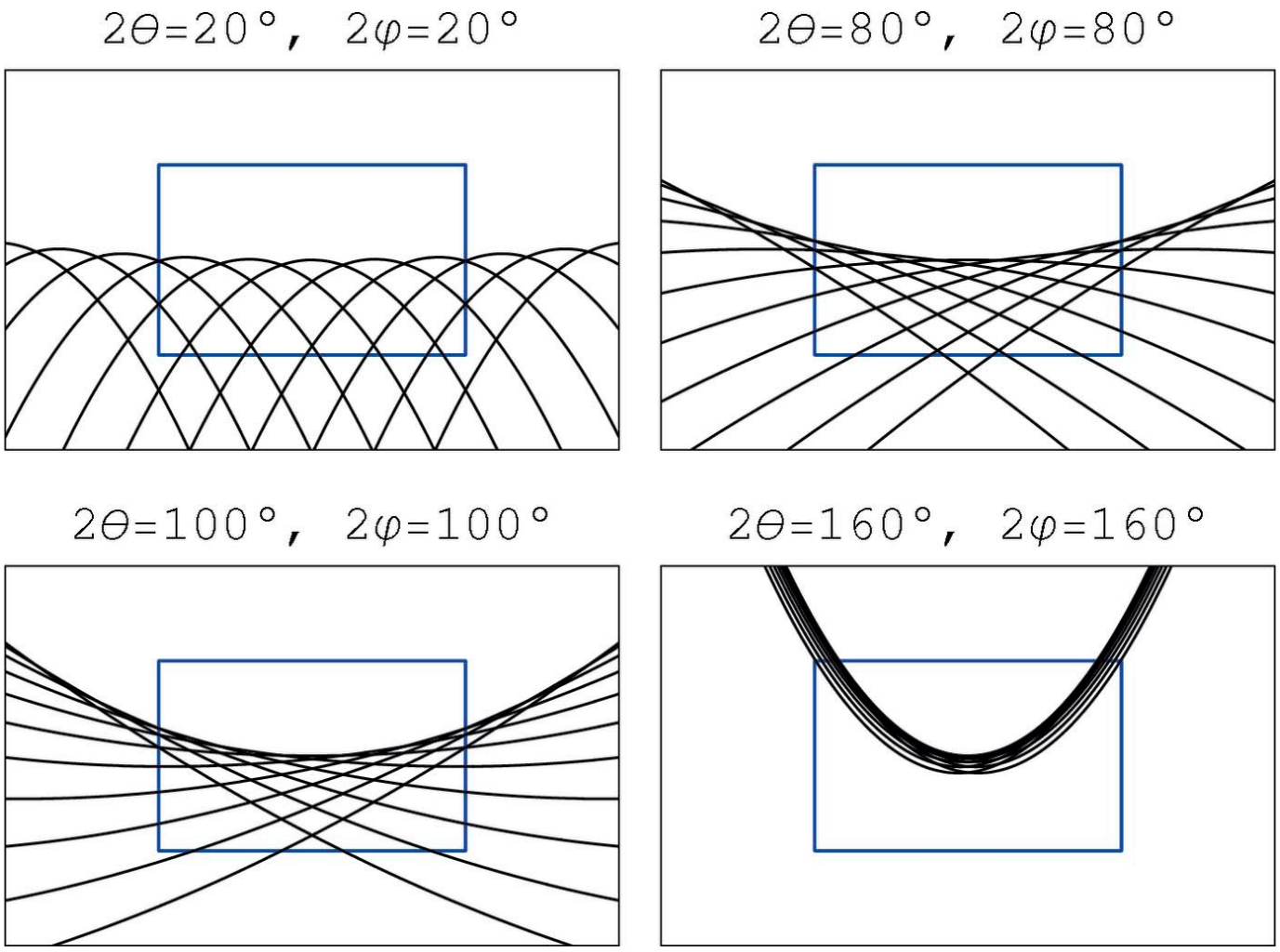
View from the top



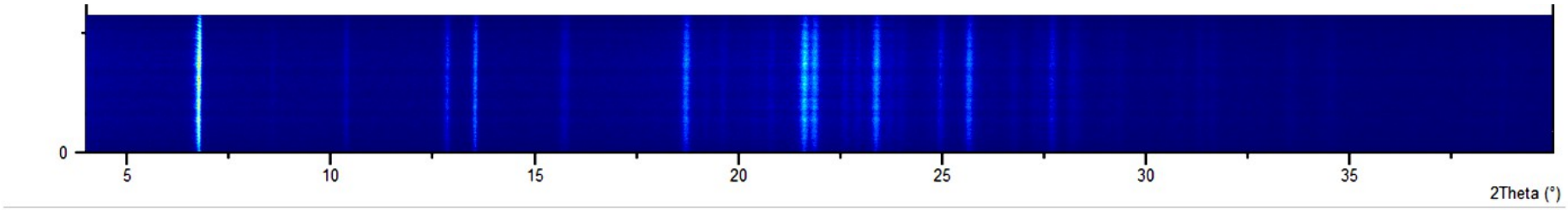
View from side



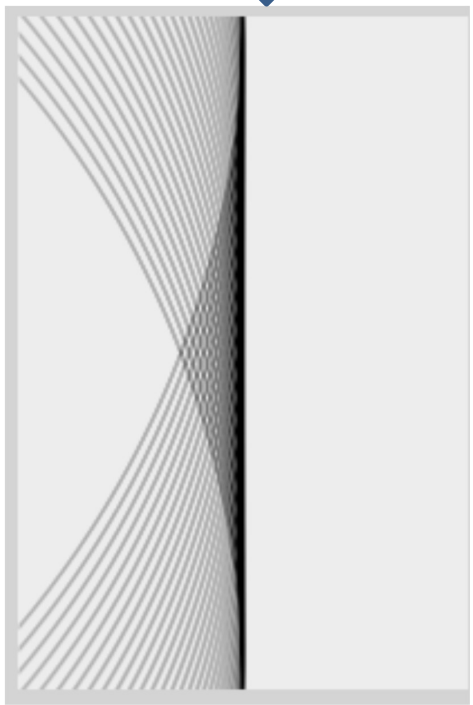
Asymmetry

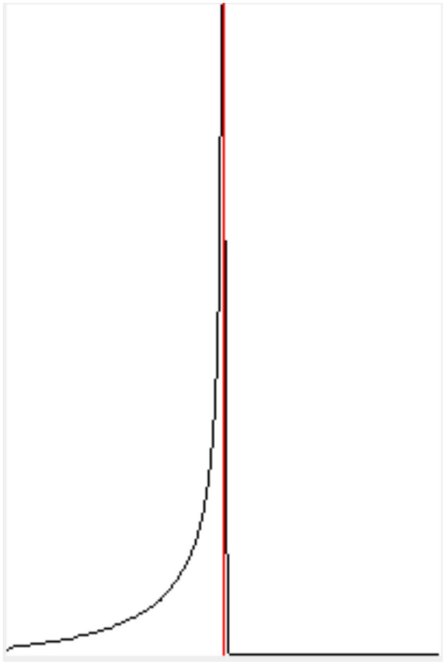


Asymmetry



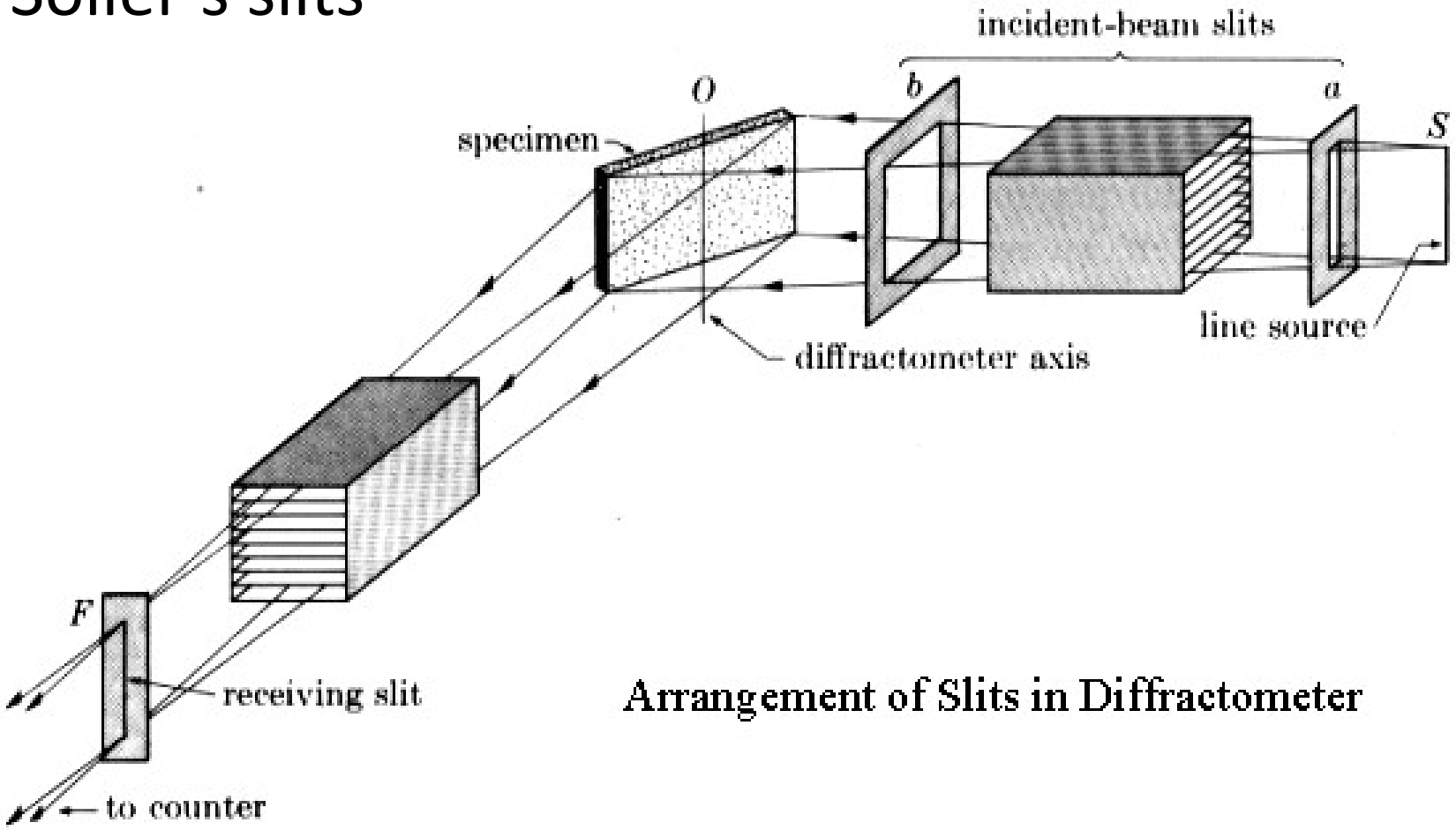
The sample is diffracting as cones…





Asymmetry

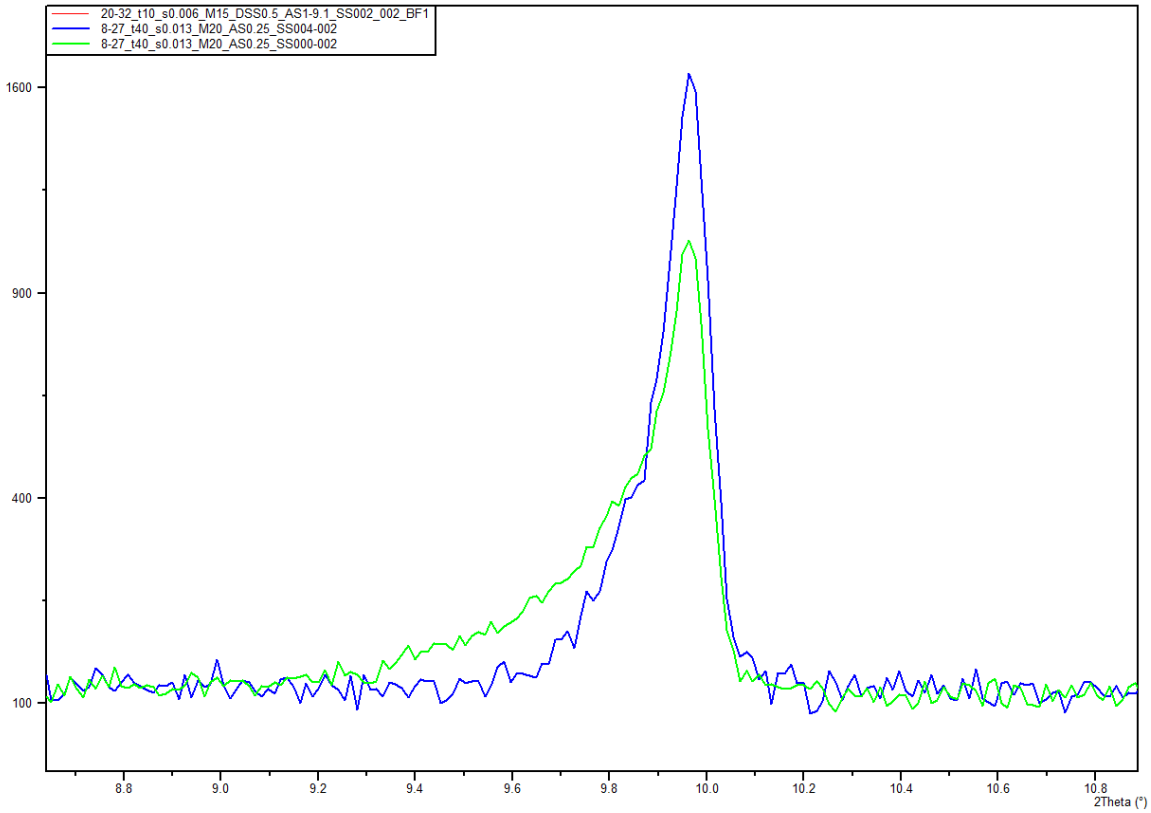
- Soller's slits



Arrangement of Slits in Diffractometer

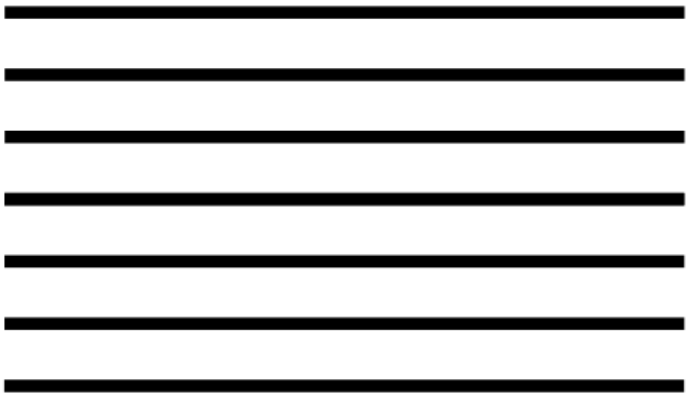
http://capsicum.me.utexas.edu/ChE386K/html/slit_arrangement.htm

Influence of the soller's slits



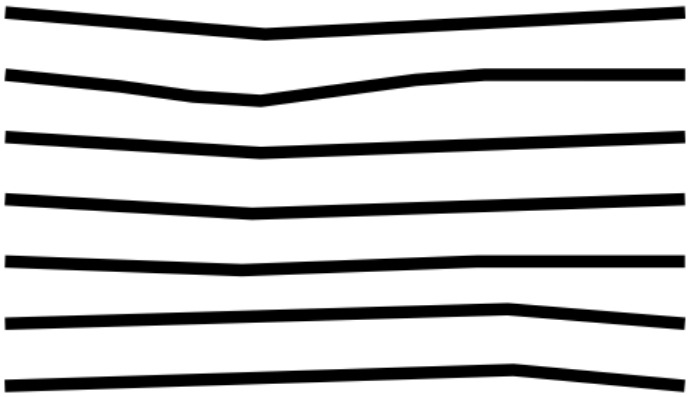
Strain

constant d_{hkl}



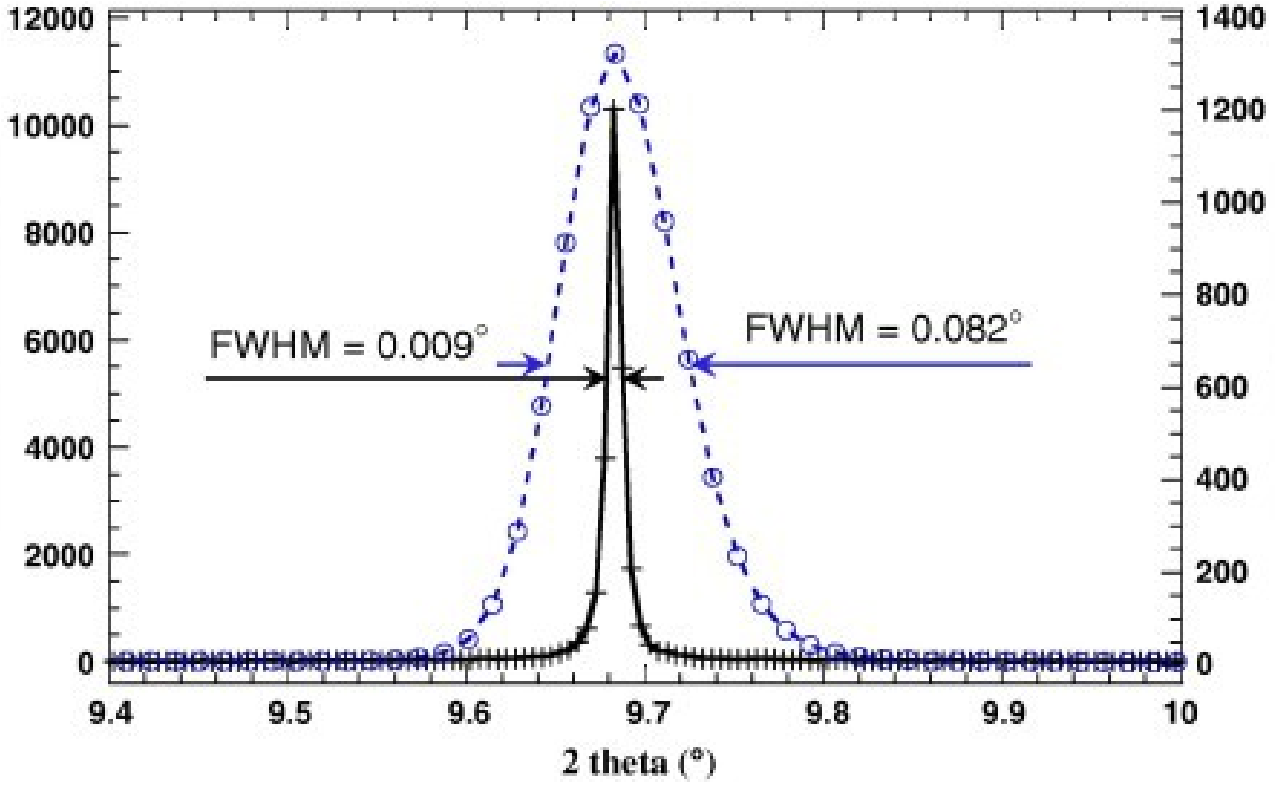
Peak width is mainly given by instrumental function

d_{hkl} is changing from $d_{min\ hkl}$ to $d_{max\ hkl}$

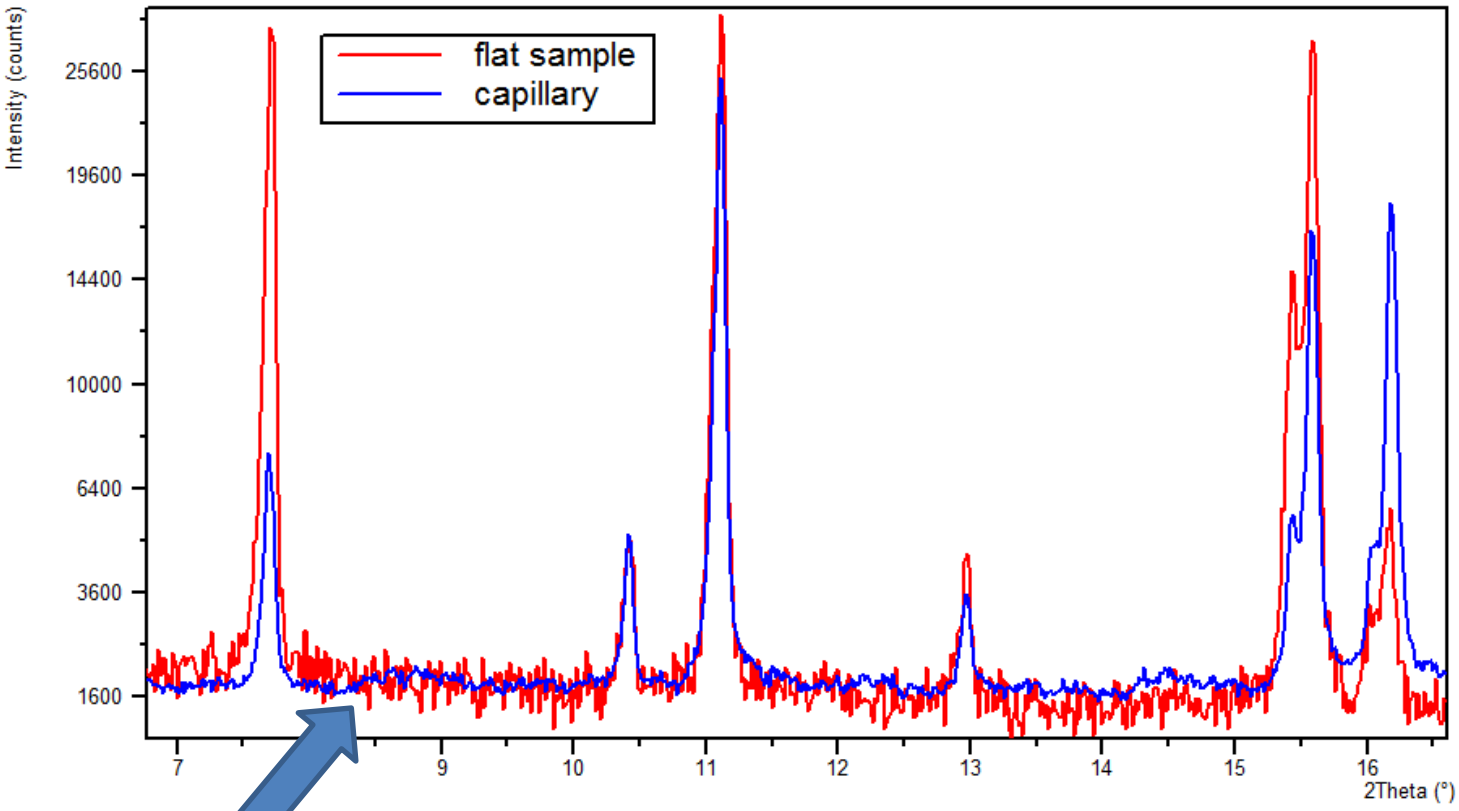


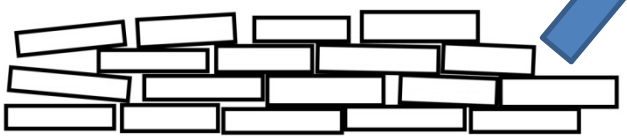
Peak width is given by instrumental function + distribution of dhkls in all single-crystals

Strain


12000
10000
8000
6000
4000
2000
0
1400
1200
1000
800
600
400
200
0
9.4
9.5
9.6
9.7
9.8
9.9
10
2 theta (°)
FWHM = 0.009°
FWHM = 0.082°

Preferred orientation





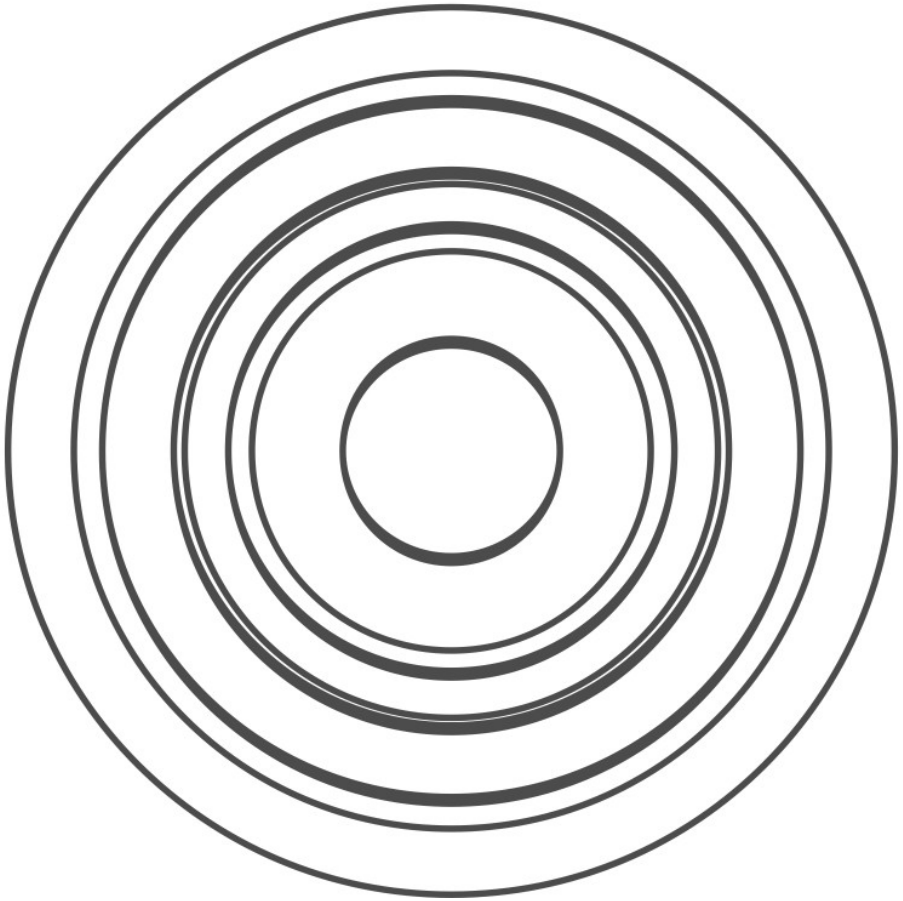
March-Dollase koeficient

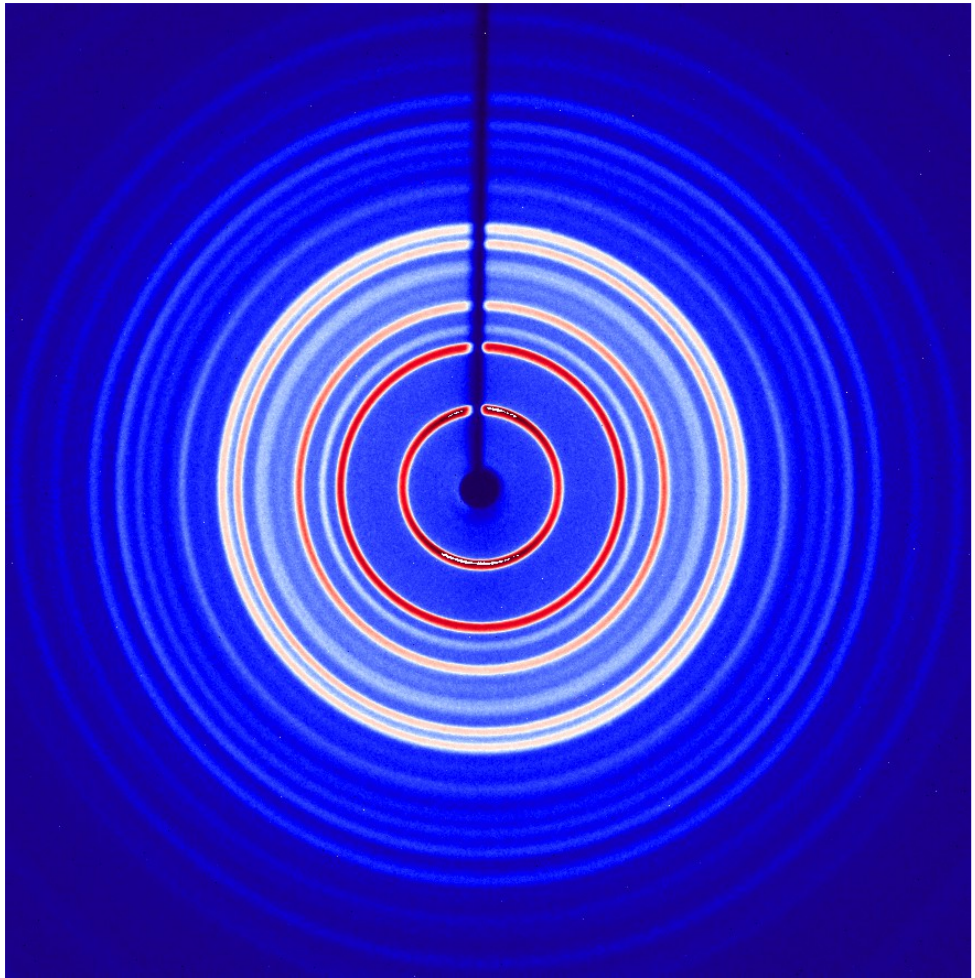
$$O_{ph} = \frac{1}{M_p} \sum_{j=1}^{M_p} \left(R_o^2 \cos^2 A_j + \frac{\sin^2 A_j}{R_o} \right)^{-3/2}$$

Angle between the direction and current direction

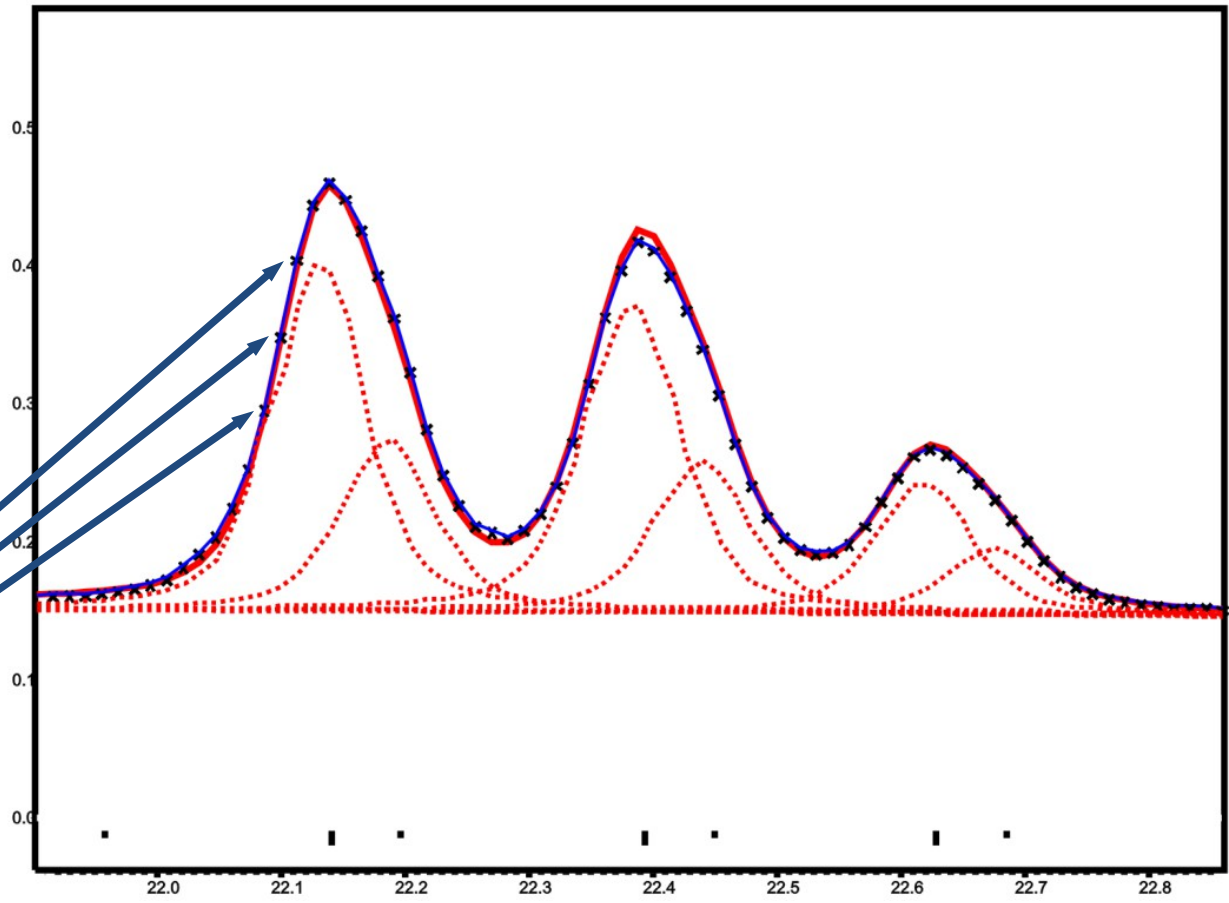
Refined parameter

Preferred orientation





Powder pattern – final equation



Intensity at every point

$$y_{ci} = s \sum_h L_h |F_h|^2 \delta(2\theta_i - 2\theta_h) P_h A + y_{bi}$$

s – scale factor, $\mathbf{L_h}$ – Lorentz, polarization and multiplicity factor,

$\mathbf{F_h}$ – structure factor, **δ** – reflection profile, $\mathbf{P_h}$ – preferred orientation function, **A** – absorption factor, $\mathbf{y_{bi}}$ - background

End

Thank you !